COMPOSITION AND PROCESS FOR THE RADICAL POLYMERIZATION OF ETHYLENICALLY UNSATURATED MONOMERS

An object of the present invention is a composition which can be used as an inhibitor of the radical polymerization of ethylenically unsaturated monomers and a process for preventing the radical polymerization of such unsaturated monomers during their industrial preparation. It relates in particular to vinyl aromatic monomers.

Ethylenically unsaturated monomers are liable to polymerize spontaneously under the action of heat. Thus, premature polymerization must be avoided during production, purification and storage of said monomers. During production or purification, premature polymerization is detrimental as it causes a drop in production yields and clogs up machinery, often making it necessary to stop production temporarily for maintenance, leading to a production surcharge. Due to the exothermicity of the polymerization reaction, explosions and fires are also of concern.

The distillation of certain ethylenically unsaturated monomers is particularly problematic as high temperatures must be used: this applies in particular to the distillation of vinylaromatic derivatives such as styrene, l'-methylstyrene and other vinylbenzenes.

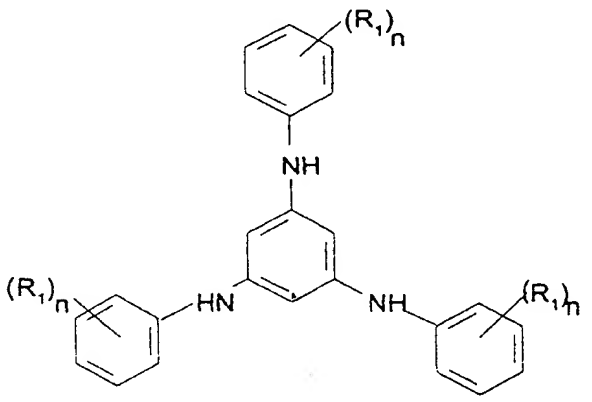
To prevent the polymerization of ethylenically unsaturated monomers, it is known in the state of the art to add one or more polymerization inhibitors or retarders, either in a preventative manner in the course of production or also directly to the said monomers before using them.

Thus, to inhibit the polymerization of styrene during its production, industry currently uses 2,4-dinitrophenol, 4,6-dinitro-o-cresol (DNOC), 2,6-dinitro-p-cresol (DNPC) [US 4 105 506] or also 2,4-dinitro-6-sec-butylphenol (DNBP). The Patent US 4 466 905 demonstrates that the combinations of 2,6-dinitro-p-cresol with p-phenylene diamine compounds or with tert-butylcatechol are very effective at limiting the polymerization of styrene if a minimum amount of oxygen is present. In JP 63 316745, the possibility of using 2-methyl-4-nitrosophenol in combination with 2,6-dinitro-p-cresol is indicated.

In general, the nitrophenolic inhibitors of the state of the art are relatively toxic and are not always very stable.

An object of the invention is to provide a composition for preventing premature polymerization of ethylenically unsaturated monomers during the production of said monomers.

An object of the present invention is therefore a composition intended to prevent the radical polymerization of ethylenically unsaturated monomers characterized in that it comprises at least one benzenetriamine derivative corresponding to general formula (I):



(I)

in said formula (I):

-the identical or different R_1 radicals represent a hydrogen atom or an electro-doner group,

-the n's, identical or different, represent a number equal to 0, 1 to 5.

A variation of the invention consists of combining the benzenetriamine derivative of the invention with one or several vehicles which are compatible with said monomer and with each of the constituents of the composition.

Another variation of the invention is to combine it with another polymerization inhibitor.

A compound corresponding to formula (I) in which the R_1 radical or radicals represent an electro-doner group is included in the composition of the invention.

In the present text, by "electro-doner group" is meant a group as defined by H.C. Brown in Jerry MARCH's work – Advanced Organic Chemistry, chapter 9, pages 243 and 244 (1985).

The following can be mentioned as examples of preferred R_1 electro-doner groups:

-a linear or branched alkyl radical, having 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl,

-a linear or branched alkenyl radical, having 2 to 6 carbon atoms, preferably 2 to 4 carbon atoms such as vinyl, allyl,

-a linear or branched alkoxy or thioether radical, having 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms such as methoxy, ethoxy, propoxy, isopropoxy, butoxy radicals, an alkenyloxy radical, preferably an allyloxy radical or a phenoxy radical,

-a radical of formula:

$-R_2-OH$

$-R_2-SH$

$-R_2-N-(R_3)_2$

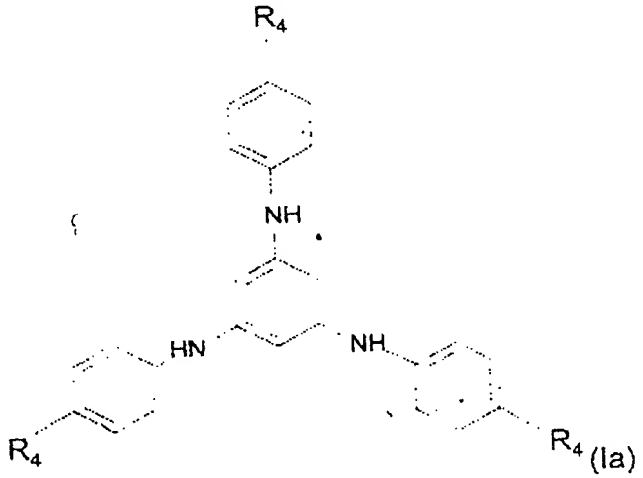
in said formulae R_2 represents a valency bond or a linear or branched, saturated or unsaturated divalent hydrocarbon radical, having 1 to 6 carbon atoms such as, for example, methylene, ethylene, propylene, isopropylene, isopropylidene; the identical or different R_3 radicals, represent a hydrogen atom or a linear or branched alkyl radical, having 1 to 6 carbon atoms.

In formula (I), n is a number preferably less than or equal to 4, preferably equal to 1 or 2.

The invention only excludes the three benzene rings carrying R_1 radicals of a different nature and whose number n is different.

Among the benzenetriamine derivatives of formula (I), certain are particularly preferred and in particular those corresponding to formula (Ia):

in said formula (Ia):



-the identical or different R_4 radicals, represent a hydroxyl group or a linear or branched alkyl or alkoxy radical, having 1 to 4 carbon atoms.

Among the compounds of formula (Ia), those which correspond to the formula (I) in which R_1 represents a hydroxy group or methoxy group or a methyl group are preferably used.

N,N',N''-tri(p-methoxyphenyl)-1,3,5-benzenetriamine and N,N',N''-tri(p-methylphenyl)-1,3,5-benzenetriamine are preferably chosen.

A mixture of benzenetriamine derivatives can also be used.

Thus, the compositions of the invention comprising at least one benzenetriamine derivative of formula (Ia) constitute a particularly preferred embodiment of the invention.

Certain benzenetriamine derivatives of formula (I) are commercially available. The others are easily prepared by a person skilled in the art using commercially-available products.

The compositions of the invention are suitable for the stabilization of any monomer having at least one ethylenic unsaturation.

Ethylenically unsaturated monomers comprise more precisely ethylenically unsaturated aromatic monomers such as styrene, α-methylstyrene, divinylbenzene, vinyltoluene, vinylnaphthalene, styrene sulphonic acids, etc.

Ethylenically unsaturated monomers also comprise olefinic monomers comprising one or two unsaturations such as isoprene and butadiene; unsaturated halogenated monomers of vinyl chloride, chloroprene, vinylidene fluoride, vinylidene chloride and vinyl fluoride type; unsaturated acids of acrylic acid, methacrylic acid and crotonic acid type; unsaturated esters, in particular unsaturated acrylic acid esters of methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate type; unsaturated methacrylic acid esters of methyl methacrylate, butyl methacrylate, lauryl methacrylate, dimethylaminoethyl methacrylate, stearyl methacrylate, vinyl acetate type; unsaturated resins such as for example acrylated epoxy resins and polyethylene glycol diacrylate; unsaturated amides such as acrylamide, N,N-dimethylacrylamide, methylene bisacrylamide and N-vinylpyrrolidone; unsaturated nitriles of acrylonitrile type; unsaturated ethers such as vinyl and methyl ether; vinylpyridines; diethyl vinylphosphonate and sodium styrene sulphonate. It should be understood that this list

is in no way exhaustive, the invention relates in a general manner to the stabilization of all types of ethylenically unsaturated aliphatic monomers.

Nevertheless, the compositions of the invention are particularly effective for the stabilization of ethylenically unsaturated aromatic monomers, in particular vinylaromatic monomers such as styrene, α-methylstyrene, divinylbenzene, vinyltoluene, styrene sulphonic acids.

The invention preferably applies to styrene.

The compositions of the invention form either true solutions, i.e. constituted by perfectly miscible ingredients, or emulsions or also suspensions. According to a preferred embodiment, the compositions are in the form of true solutions.

The presence in the composition of one or more vehicles is optional. It can prove necessary, however, when the solubility of the benzenetriamine derivatives of the composition in the monomer to be stabilized is low, indeed insufficient. In this case in fact, it is preferable to incorporate into the composition one or more vehicles which are compatible on the one hand with the monomer to be stabilized and on the other hand with each of the other constituents of the composition. By "compatible" is meant according to the invention a vehicle which is chemically inert vis-à-vis the different ingredients of the composition and the monomer. The nature of the vehicle therefore depends on the different constituents present as well as the nature of the monomer itself.

When the monomer is a vinyl aromatic derivative, particularly appropriate vehicles are benzene, toluene, xylene, ethylbenzene, styrene, acetophenone, methylphenylcarbinol or mixtures of these solvents. In this case, ethylbenzene is preferably used.

Depending on the nature of the monomer, a person skilled in the art will easily determine the combination of the benzenetriamine derivative and solvents which gives the best results.

According to the invention, it is possible to combine the benzenetriamine derivative with other standard compounds used as polymerization retarders or other polymerization inhibitors.

The choice of these is easily determined by a person skilled in the art. It depends on the nature of the polymer. Examples are given hereafter but are in no way limitative.

In the case of an ethylenically unsaturated aromatic monomer, the compositions according to the invention advantageously contain one or more nitroaromatic derivatives. Such compounds are known in the state of the art as polymerization retarders. It is also known to combine them with polymerization inhibitors. Specifically, the polymerization inhibitor prevents polymerization up to a certain time beyond which the polymerization reaction starts as normal. This time is the induction time. The longer the induction time, the more effective the inhibition. The role of the retarder is different. It does not prevent the polymerization but slows down the polymerization kinetics. A more or less significant synergy is observed in the combination of an inhibitor with a retarder. Thus, the compositions of the invention containing at least one polymerization retarder and at least one polymerization inhibitor form a preferred subject of the invention.

The nitroaromatic derivative is advantageously selected from 1,3-dinitrobenzene, 1,4-dinitrobenzene, 2,6-dinitro-4-methylphenol, 2-nitro-4-methylphenol, 2,4-dinitro-1-naphthol, 2,4,6-trinitrophenol (picric acid), 2,4-dinitro-6-methylphenol, 2,4-dinitrochlorobenzene, 2,4-dinitrophenol, 2,4-dinitro-6-sec-butylphenol, 4-cyano-2-nitrophenol and 3-iodo-4-cyano-5-nitrophenol.

2,6-dinitro-4-methylphenol, 2,4-dinitro-6-methylphenol, 2,4-dinitrophenol and 2,4-dinitro-6-sec-butylphenol are preferably used, 2,4-dinitro-6-sec-butylphenol being particularly advantageous.

The nitroaromatic derivatives are added to the composition so that the ratio of the total mass of the constituents of benzenetriamine type of formula (I) to the total mass of the nitroaromatic-type constituents is comprised between 90/10 and 10/90, preferably between 80/20 and 20/80, better still between 60/40 and 40/60. This weight ratio is calculated by determining the ratio of the total quantity (by weight) of the benzenetriamine derivatives of formula (I) present in the composition to the total quantity (by weight) of the nitroaromatic derivatives of the composition.

According to a variation of the invention, the compositions of the invention can contain other polymerization inhibitors such as alkylated phenols such as tert-buty-catechol, 2,5-di-tert-octylhydroquinone, 3,5-di-tert-octylcatechol; compounds of nitroxide type such as 2,2,6,6-tetramethylpiperidine-N-oxyl, 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl, 4-oxo-2,2,6,6-tetramethylpiperidine-N-oxyl; 4-amino-2,2,6,6-tetramethylpiperidine-N-oxyl; imidazolidines/imidazolines-N-oxyl as described in FR 97/04230, preferably 2,2,3,4,5,5-hexamethylimidazolidine-1-oxyl or

any other inhibitors known in the state of the art provided that they are compatible with the other ingredients of the composition under the operating conditions to which the monomer to be stabilized is subjected.

In the case of an ethylenically unsaturated aliphatic monomer, it is also possible to use other inhibitors such as hydroquinone, p-methoxyphenol, phenothiazines.

The standard polymerization inhibitor or inhibitors are added to the composition such that the ratio of the total mass of the constituents of benzentriamine type of formula (I) to the total mass of the other inhibitors is comprised between 90/10 and 10/90, preferably between 80/20 and 20/80, better still between 60/40 and 40/60.

The compositions of the invention are easily prepared by mixing the different constituents in the selected vehicle.

Another object of the invention is a process allowing the prevention of the radical polymerization of an ethylenically unsaturated monomer preferably a vinyl aromatic monomer. This process comprises, for example, the addition to said monomer of an effective quantity of a composition of the invention as defined above.

The quantity of benzenetriamine derivative to be added in order to obtain an effective inhibition of the polymerization varies greatly. It is a function of the monomer to be stabilized and operating conditions to which this monomer is subjected. It is clear that at high temperatures, the quantity of inhibitor becomes more significant. The process of the invention is in fact applicable for the stabilization of the monomer during production and purification. Therefore, it is common for the purification to be carried out by distillation of the monomer, the temperature at boiling point being able to exceed 120°C.

Thus, the ideal quantity of inhibitor must be evaluated case by case.

Whatever this may be, by way of indication, a total quantity of benzenetriamine derivative comprised between 1 and 2000 ppm, preferably between 5 and 1000 ppm generally suffices, this quantity being expressed relative to the total weight of the monomer to be stabilized.

As indicated previously, it is desirable to add to the ethylenically unsaturated aromatic monomer an effective quantity of one or more nitroaromatic derivatives as a polymerization retarder. As a preferred retarder, 2,6-dinitro-4-methylphenol, 2,4-

dinitro-6-methylphenol and 2,4-dinitrophenol, but above all 2,4-dinitro-6-sec-butylphenol can be mentioned again.

The proportion of the nitroaromatic-type retarder or retarders is preferably such that the ratio of the total mass of the benzenetriamine-type constituents of formula (I) to the total mass of nitroaromatic-type constituents is comprised between 90/10 and 10/90, better still between 80/20 and 20/80. This weight ratio is calculated by determining the ratio of the total quantity (by weight) of benzenetriamine derivatives of formula (I) present in the composition to the total quantity (by weight) of nitroaromatic derivatives of the composition.

As previously indicated, it is possible to add one or more known polymerization inhibitors to the monomer.

The proportion of the polymerization inhibitor or inhibitors is preferably such that the ratio of the total mass of constituents of benzenetriamine derivative type of formula (I) to the total mass of other inhibitors is comprised between 90/10 and 10/90, better still between 80/20 and 20/80.

The benzenetriamine derivative according to the invention, optionally combined with a nitroaromatic derivative or other standard polymerization inhibitors can be added to the monomer in a completely conventional manner. The point of introduction, in the case of a distillation, is very variable: it can be envisaged to add each of these compounds at the level of heat exchangers, pipes, pumps, boilers, compressors or more generally containers. It should be understood that the addition can be carried out continuously or also repeated over time at one or different specific sites.

According to the invention, it is possible to envisage the simultaneous or separate addition of the inhibitor of the invention and/or the retarder and/or the other inhibitor.

The process of the invention is particularly advantageous in terms of the effectiveness of inhibition of the radical polymerization of aromatic vinyl monomers.

The following examples are given by way of illustration and relate to the preferred embodiments of the invention.

EXAMPLES OF USE ON AROMATIC VINYL MONOMERS

Example 1

Comparison Example 1a

In order to evaluate the inhibition properties of the products of the invention referenced vis-à-vis the radical polymerization of vinyl monomers, inhibition tests with styrene were carried out with the following operating protocol.

Before each test, the styrene used (marketed by Merck) is first destabilized by passing it over an activated alumina column (obtained from Procatalyse) in order to completely eliminate the tert-butylcatechol initially present at a rate of 15-20 ppm.

The resulting styrene (10 ml) is placed in a test tube and the adequate quantity of inhibitor is then added.

Argon is introduced in the liquid phase of the reactor by bubbling through (5 mins) as well as in the top of the reactor by bubbling through (5 mins).

The tube is closed and placed in an oil bath thermostatically controlled at 100°C for 2 hours.

The amount of polymer formed after 2 hours is determined by the precipitation process from methanol.

To this end, a cooled-down sample of 10 ml of styrene is decanted into a glass flask containing approximately 50 ml of methanol in order to precipitate the polystyrene formed which is insoluble in the methanol.

The precipitate is then filtered on a milliporous filter then the residue is dried in a stove at 40°C before being weighed.

The results of the tests are summarized in Table (I).

Table (I)

Ref. ex.	Inhibitor	Content relative to the styrene (ppm)	Amount of polymer formed
1a	no inhibitor	0	5.72
1	N,N',N"-tri(p-methoxyphenyl)-1,3,5-benzenetriamine	100	0

The results show that the benzenetriamine derivatives are excellent inhibitors of the polymerization of styrene.

EXAMPLES OF USE ON UNSATURATED ALIPHATIC MONOMERS

In order to evaluate the inhibitory properties of the products of the invention vis-à-vis the radical polymerization of unsaturated aliphatic monomers, inhibition tests with methyl methacrylate were carried out with the following operating protocol.

The effectiveness of an inhibitor according to the invention (or a mixture of inhibitors including at least one inhibitor according to the invention) for methyl methacrylate is determined by measuring the induction time which represents the time at the end of which the monomer starts to polymerize when it is heated in a bath at regulated temperature and in the presence of an initiator. This time is determined by a slight exothermicity of the sample studied.

The measures are carried out in a laboratory calorimeter, the time and temperature parameters are recorded and transferred to a microcomputer.

The tests were carried out with methyl methacrylate (MMA) previously destabilized by passing over an activated alumina column in order to completely eliminate the p-methoxyphenol (initial stabilizing agent) from the medium.

20 ml of MMA restabilized with 20 ppm of the inhibitor to be tested is introduced into a test tube then 100 ppm of azobisisobutyronitrile (AIBN) initiator is introduced. The tube is immersed in a bath thermostatically controlled at 80°C and the difference in temperature between this sample and a reference tube containing silicone fluid is recorded continuously. The induction time Ti corresponds to the visible exothermicity which indicates the start of the MMA polymerization. The curve T as a function of time is recorded continuously. The greater the induction time, the more effective the inhibitor tested is at a constant weight concentration.

The following Table (II) shows the induction time values of some "standard" industrial (meth)acrylate inhibitors.

Table (II)

Inhibitors	Induction time Ti (min)
phenothiazine (PTZ)	26
hydroquinone (HQ)	55

Examples 2 and 3

The operating protocol given above is repeated for each polymerization inhibitor.

Table (III) summarizes the results obtained over the induction times for different inhibitors of the invention.

Table (III)

ref. ex.	Polymerization inhibitors	Induction time Ti (min) of MMA
2	N,N',N"-tri(p-methylphenyl)-1,3,5-benzenetriamine	70
3	N,N',N"-tri(p-methoxyphenyl)-1,3,5-benzenetriamine	53

The induction time values are better than or equivalent to hydroquinone which is currently one of the best industrial inhibitors for the (meth)acrylates industry.

Example 4

In this example, the combination of N,N',N"-tri(p-methoxyphenyl)-1,3,5-benzenetriamine of the invention with another inhibitor is described.

In the test, 20 ml MMA + 100 ppm AIBN + a mixture of inhibitors: 10 ppm hydroquinone (HQ) + 10 ppm inhibitor of the invention are used.

Table (IV) summarizes the results obtained over the induction time for the mixture of the inhibitors of the invention.

Table (IV)

Ref. ex.	Inhibitor	Induction time Ti (min) of MMA
4	HQ + N,N',N"-tri(p-methoxyphenyl)-1,3,5-benzenetriamine	65